UDC 666.189.3:536.4

KINETICS OF FORMATION OF THE POROUS STRUCTURE IN FOAM GLASS

V. A. Lotov[1] and E. V. Krivenkova[1]

The results of studying the production of foam glass based on container, sheet, and lamp glass cullet and their mixture are described. The possibility of using the parameters obtained from the correlation of the relative density and porosity of the initial and the final state of the material for predicting, control, and kinetic research of pore formation in foam glass is demonstrated. Formulas for processing kinetic data and calculating the thermophysical properties of a batch are proposed.

Due to a fortunate combination of unique properties, foam glass is currently the most promising heat-insulating material, whose production in Russia has to be resumed in the nearest future. Such properties of foam glass as longevity, i.e., the ability to withstand various factors for a long time, makes it possible to satisfy the main principle of selection and application of a heat-insulating material, that is, the service life of the heat-insulating material should be equal or comparable to the service life of the structural material used in the construction of the particular building.

Furthermore, production of foam glass provides an effective solution of the cullet utilization problem [1], since the color of glass has no significant effect on the foam glass quality. However, the differences in the chemical composition and, accordingly, the different properties of the cullet generated by container, sheet, or lamp glass have an effect on pore formation in foam-glass batches prepared from the particular types of glass. In spite of the long history of the foam-glass technology [2], the best studied method involves the use of sheet glass cullet in foam glass production [3], and there is yet no reliable method for the evaluation and prediction of the pore-formation process in foam glass.

The purpose of the present study was to apply the earlier proposed approaches [4, 5] involving volume phase parameters or their combinations to evaluate the foaming process in foam-glass batches prepared from container, sheet, or lamp cullet, or their mixture.

The essence of these approaches is that a foam-glass batch is a two-phase disperse system (S + G) initially consisting of certain volume quantities of the solid phase K_{s_1}

and free pore space ($P_1 = 1 - K_{s_1}$). When such a system is subjected to an external thermal effect, it passes from the sta-

tionary state into a dynamic state, in which the physico-chemical processes of sintering and subsequent pore formation take place with a respective modification of the ratio between the volume concentrations of the solid phase and free pore space. After the external thermal effect is removed, the system, as a consequence of the quantitative modifications, acquires a new qualitative state, which in its final stage is characterized by the values K_{s_2} and P_2, equal to $1 - K_{s_2}$. In this case the level and the type of variations that have taken place within the system can be estimated based on the structure-energy parameter n:

$$\frac{K_{s_2}}{P_2} = n \frac{K_{s_1}}{P_1},\qquad(1)$$

where K_s is the volume concentration of the solid phase, relative units; $K_s = \rho_s / \rho_{tr}$ (ρ_s is the apparent density of the batch layer; ρ_{tr} is the true density of glass, kg/m^3; $\rho_{tr_1} = \rho_{tr_2}$).

If no changes occur within the system, then $n = 1$. A decrease in the volume (shrinkage) of the system is characterized by $n > 1$, and a volume increase (swelling) is characterized by $n < 1$. Useful information on the modification of the material structure can be obtained by normalizing the parameter n within the limits of $(0 – 1)$. In the case of condensation of the material, the degree of structural modification α_n is determined from the formula

$$\alpha_n = \frac{n_i - n_1}{n_i} = \frac{n_i - 1}{n_i},$$

where n_i is the current value of the parameter n in the course of consolidation; n_1 is the value of the parameter n for the initial state of the system; $n_1 = 1$.

---

[1] Tomsk Polytechnical University, Tomsk, Russia.
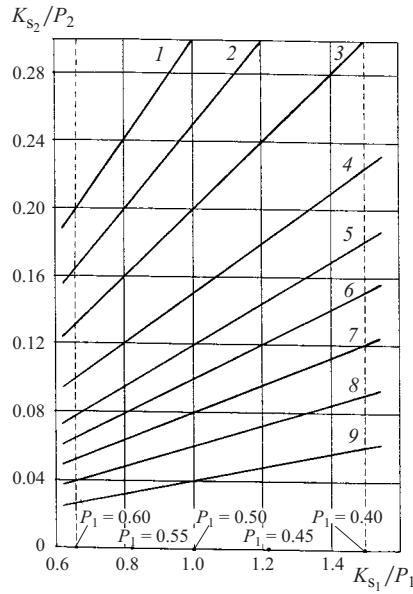
Fig. 1. Relationship between the structural parameters of the initial and the final states of a system rendered porous: *1*) $n = 0.30$, $\alpha_n = 0.70$; *2*) $n = 0.25$, $\alpha_n = 0.75$, $1/n = 4.0$; *3*) $n = 0.20$, $\alpha_n = 0.80$, $1/n = 5.0$; *4*) $n = 0.15$, $\alpha_n = 0.85$, $1/n = 6.6$; *5*) $n = 0.12$, $\alpha_n = 0.88$, $1/n = 8.3$; *6*) $n = 0.10$, $\alpha_n = 0.90$, $1/n = 10.0$; *7*) $n = 0.08$, $\alpha_n = 0.92$, $1/n = 12.5$; *8*) $n = 0.06$, $\alpha_n = 0.94$, $1/n = 16.6$; *9*) $n = 0.04$, $\alpha_n = 0.96$, $1/n = 25.0$.

The degree of material restructuring in pore formation is determined from the relationship

$$\alpha_n = \frac{1/n_i - 1}{1/n_i} = 1 - n_i, \qquad (2)$$

where $1/n_i$ is the swelling of the material during or after impact on the disperse system; $1/n_i = V_2/V_1$ (V_2 and V_1 are the volumes of the system in its final and initial state, m³).

Setting different values of the porosity or volume concentration of the solid phase in the batch layer in the initial state within the limits of $P_1 = 0.45 - 0.60$, $K_{s_1} = 0.55 - 0.40$ and making simple computations for glass with a true density of 2500 kg/m³, we obtain the following structure modification parameters in producing foam glass of a preset density (Table 1).

As can be seen, the smaller the value of the parameter n in the transition of a system from its initial state to its final state, the more intense are the processes of pore formation and structural modification in the particular material. This, in turn suggests an important practical conclusion for foam glass technology: the better and the more uniform is the compression of a batch in the foaming molds, the higher the probability (all other conditions being equal) of getting foam glass with a lower density and a homogeneous structure.

Based on ratio (1), the relationship of the restructuring parameters in pore formation and foam glass production can be graphically represented (Fig. 1). Using this relationship and the linear dependence between the swelling of a material $1/n$ and the specific volume of the foam glass $1/\rho_{fg}$, the relationship between the parameter n and the density of the obtained foam glass ρ_{fg} for the preset structural characteristics of the batch layer in the initial state (K_{s_1}, P_1) can be found from the formula

$$\rho_{fg} = \frac{\rho_{tr} n K_{s_1}}{P_1 + n K_{s_1}}. \qquad (3)$$

The current density of foam glass in the process of pore formation can also be calculated from the formula

$$\rho_{fg} = \rho_{tr} K_{s_2}.$$

It should be noted that the dependence $\rho_{fg} = f(\alpha_n)$ consists of two rectilinear segments with different angle coeffi-

TABLE 1

Structure modification parameters	Foam glass density, kg/m³										
	100	150	200	250	300	350	400	450	500	550	600
K_{s_2}	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24
P_2	0.96	0.94	0.92	0.90	0.88	0.86	0.84	0.82	0.80	0.78	0.76
n_i for P_1:											
0.45	0.034	0.052	0.071	0.091	0.111	0.133	0.156	0.179	0.204	0.231	0.258
0.50	0.042	0.064	0.087	0.111	0.136	0.162	0.190	0.219	0.250	0.282	0.315
0.55	0.051	0.078	0.106	0.136	0.166	0.199	0.233	0.268	0.305	0.344	0.385
0.60	0.062	0.096	0.130	0.166	0.204	0.244	0.285	0.329	0.375	0.423	0.473
$1/n_i$ for P_1:											
0.45	29.32	19.23	14.08	10.99	9.01	7.52	6.41	5.58	4.90	4.33	3.87
0.50	24.03	15.67	11.50	9.00	7.35	6.17	5.26	4.56	4.00	3.54	3.17
0.55	19.64	12.82	9.43	7.35	6.02	5.02	4.29	3.73	3.28	2.91	2.59
0.60	16.00	10.45	7.69	6.02	4.90	4.10	3.51	3.04	2.66	2.36	2.11
α_n for P_1:											
0.45	0.966	0.947	0.929	0.909	0.888	0.867	0.844	0.820	0.795	0.769	0.742
0.50	0.958	0.936	0.913	0.888	0.863	0.837	0.809	0.780	0.750	0.718	0.684
0.55	0.949	0.922	0.894	0.864	0.833	0.801	0.767	0.732	0.694	0.655	0.614
0.60	0.937	0.904	0.869	0.833	0.795	0.756	0.714	0.670	0.625	0.577	0.526

cients and a break point corresponding to $\rho_{fg} = 400$ kg/m³. This is evidence of the different mechanisms and intensities of the pore-forming process before and after the specified density regardless of the initial porosity of the batch.

Revealing the specifics and the structure-formation kinetics for batches prepared from different types of cullet is a sufficiently complicated problem, whose solution is determined by the selection of a dependent variable or an evaluation parameter for the pore-formation process. It is proposed to use the degree of structural modification α_n in pore formation found from formula (2) for this purpose.

The gas-forming agent in the experiment was activated low-ash charcoal that virtually did not contain volatile compounds. Coal was introduced in the batch in the amount of 1%. To determine the effect of the quantity of the gas-forming agent on the pore formation process, batches based on container glass were prepared with a coat content equal to 1.5, 2.0, and 2.5%. Joint milling of glass and the gas-forming agent was performed in a ball mill with metal milling bodies to obtain a specific surface area of the batch within the range of 600 – 610 m²/kg (air permeability, a PSKh-2 unit). The kinetics of pore formation in the batch was analyzed using a Shill instrument [6] with the inner diameter of the metal cylinder equal to 48 mm, height 85 mm, and wall thickness 3 mm.

To prevent the adhesion of foam glass to the mold walls and bottom, they were preliminary coated with a clay paste. After drying, a batch sample of 20 g was poured into the mold, and the layer was leveled on the upper surface and compacted, if necessary. The porosity of a freely poured layer is 60% ($P_1 = 0.6$) and after the layer was compressed by the punch, the porosity was equal to 51% ($P_1 = 0.51$). These porosity levels were accepted as the initial values for all batches investigated.

The cartridge with the batch inside was placed in a laboratory shaft furnace preheated to a temperature of 800, 820, 840, and 860°C. The volume variations in the batch under heating were registered on a millimeter scale using a nichrome rod 1 mm in diameter, whose upper part penetrated the central opening in the cartridge lid and protracted to about 20 mm above the furnace lid, whereas the lower part of the rod was twisted into an Archimedean spiral (to decrease the impact on the pyroplastic material).

Based on the obtained data, the values of the parameters n_i, K_{s_1}, $1/n_i$, and α_{ni} were calculated. As it is impossible within the scope of the present paper to represent all data on pore formation in 14 batches at four different temperatures, the following regularities of the process should be noted:

– the pore formation process consists of three stages: heating, shrinkage in sintering, and subsequent swelling of the batch;

– regardless of the heating temperature and the batch composition, the heating duration is 9 – 11 min;

– during shrinking the batch porosity decreases: in heating batches with an initial porosity of $P_1 = 0.6$, the final po-

TABLE 2

K_s	P	ρ_s, kg/m³	λ, W/(m · K)	c, kJ/(kg · K)	$a \times 10^4$, m²/sec
0.40	0.60	1000	0.310	0.868	3.57
0.45	0.55	1125	0.346	0.851	3.61
0.50	0.50	1250	0.382	0.835	3.66
0.55	0.45	1375	0.418	0.818	3.71
0.63	0.37	1575	0.475	0.792	3.80

rosity after shrinking is $P_2 = 0.5$, and for the batches with $P_1 = 0.5$, $P_2 = 0.37$;

– as the temperature increases, the duration of isothermal pore formation becomes significantly shorter.

An analysis of the structural modification in pore formation in foam-glass batches according to formula (3) indicated that preliminary compaction and a decreased initial porosity may even delay the beginning of pore formation. Consequently, the modification of the ratio between the solid and the gaseous phases in the system due to compaction does not determine completely the batch behavior in the course of pore formation.

The calculations demonstrate that the phase ratio primarily determines the thermophysical parameters of the batches, whose values can be computed using the additivity rule:

$$\begin{cases} \lambda = K_s\lambda_s + P\lambda_g; \\ c = K_s c_s + P c_g; \\ a = \lambda / c\rho_s, \end{cases} \qquad (4)$$

where λ, c, and a are the thermal conductivity, specific heat, and thermal conductivity of the batches; λ_s, c_s and λ_g, c_g are the parameter values for the solid and the gaseous phases, respectively; K_s and P are the volume parts of the solid and the gaseous phases.

The results of calculation of the thermophysical properties of the batch at 20°C are shown in Table 2. The following values were taken for these calculations: $\lambda_s = 0.742$ W/(m · K), $c_s = 0.67$ kJ/(kg · K), $\lambda_g = 0.024$ W/(m · K), $c_g = 1.0$ kJ/(kg · K).

These data are rather approximate, as the values of true density, thermal conductivity, and heat capacity depend on the glass composition and the temperature, and as the temperature increases, the specified properties are modified due to the changed state of aggregation of the glass and changes in the gas phase composition. However, the pore formation process is determined by the thermophysical properties of the batch and primarily by the thermal conductivity of the batch, which significantly increases after compaction.

The kinetic data of the compaction process also indicate a positive effect of preliminary compaction on the pore formation process (Table 3). The obtained data were processed using the equation

$$\alpha_n = 1 - e^{-k \ln \tau} e^b \text{ or } \ln(1 - \alpha_n) = -k \ln \tau + b, \qquad (5)$$

where $0 < \alpha_n < 1$; k is the pore-formation rate constant, min⁻¹.
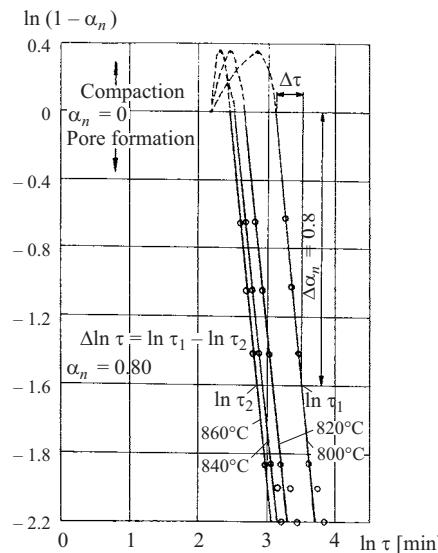
Fig. 2. Pore formation kinetics for batch 11 and data for the calculation of its apparent activation energy and the process rate.

The apparent activation energy of the pore formation process in batches E_p was determined using the coordinate section method (Fig. 2) recommended in [7]. Graphic dependences based on the obtained data were plotted in the coordinates of $\ln(1 - \alpha_n) = f(\ln \tau)$, and the activation energy for the values $\ln(1 - \alpha_n) = -1.61$, $\alpha_n = 0.8$ for all batches was calculated using the formula

$$E_p = \frac{R(\ln\tau_1 - \ln\tau_2)}{1/T_1 - 1/T_2},$$

where R is the universal gas constant, $R = 8.314$ J/(mole · K); τ_1, τ_2 is the time of reaching the value $\alpha_n = 0.8$ for the respective temperatures, min; $T_1 = 1073$ K; $T_2 = 1133$ K.

The value of $\alpha_n = 0.8$ was selected due to the fact that experimental data within the interval of $\alpha_n = 0 - 0.8$ satisfy Eq. (5), and for the values $\alpha_n > 0.85 - 0.90$, a deviation from the linear dependences is observed in some batches, which points to a modification of the pore formation mechanism.

The value interval of $E_p = 84 - 168$ kJ/mole correlates with the apparent activation energy of a viscous flow, and this mechanism is predominant in pore formation. Analysis of the data in Table 3 suggests the following conclusions:

– preliminary compaction of batches facilitates a decrease in the activation energy of pore formation;

– based on the pore formation rate, batches prepared from different types of cullet and 1% gas-forming agent can be ranked in the following sequence: lamp glass > sheet glass > glass mixture > container glass;

– an increase in the amount of the gas-forming agent in the batch increases the pore formation rate and significantly decreases the activation energy of the process.

Studies of the texture (a MBS-9 microscope) of foam glass made of container cullet demonstrated that the size of the main bulk of the pores and the partition thickness depend on the pore formation temperature, the process duration, and the amount of the gas-forming agent introduced. Thus, in the temperature range of $800 - 860°C$, the pore size increases from $0.5 - 2.4$ to $1.9 - 6.0$ mm in batch 2, from $0.6 - 4.2$ to $5.0 - 8.0$ mm in batch 4, and from $0.75 - 4.4$ to $7.0 - 9.0$ mm in batch 8. Due to the small volume of the system investigated, the pore size along the sample height is unequal and grows from the bottom to the top of the sample. The emergence of large pores in the upper part of the samples can be caused by coalescence of pores due to local overheating and a decrease in the glass viscosity. The coalescence of pores is the reason for the deviations of the experimental data in the linear dependence of $\ln(1 - \alpha_n) = f(\ln \tau)$ with $\alpha_n > 0.85$.

TABLE 3

Batch	Glass cullet*	Amount of glass-forming agent, %	Initial porosity of layer, rel. units	$\Delta\ln\tau$ at $\alpha_n = 0.8$	Time of the start of pore formation $\ln\tau$, min ($\alpha_n = 0$), at temperature		Pore formation rate $10^2 (\alpha_n/\Delta\tau)$, min^{-1}	Apparent activation energy, kJ/mole
					800°C	860°C		
1	CG	1.0	0.51	4.25 – 3.45 = 0.80	3.65	2.75	2.53	134.9
2	CG	1.0	0.60	4.40 – 3.40 = 1.00	3.75	2.83	2.05	168.6
3	CG	1.5	0.51	3.85 – 3.04 = 0.81	3.45	2.87	5.16	136.6
4	CG	1.5	0.60	4.00 – 3.00 = 1.00	3.52	2.72	3.84	168.6
5	CG	2.0	0.51	3.75 – 3.10 = 0.65	3.35	2.75	5.71	109.6
6	CG	2.0	0.60	3.85 – 3.00 = 0.85	3.40	2.64	4.69	143.3
7	CG	2.5	0.51	3.55 – 3.05 = 0.40	3.17	2.75	7.27	84.3
8	CG	2.5	0.60	3.55 – 3.05 = 0.40	3.20	2.70	7.78	84.3
9	SG	1.0	0.51	3.97 – 3.25 = 0.72	3.35	2.75	3.26	121.4
10	SG	1.0	0.60	3.85 – 3.25 = 0.60	3.30	2.75	4.02	101.2
11	LG	1.0	0.51	3.50 – 2.85 = 0.65	3.10	2.45	7.31	109.6
12	LG	1.0	0.60	3.60 – 2.85 = 0.75	3.15	2.50	6.01	126.5
13	GM	1.0	0.51	3.65 – 3.00 = 0.65	3.05	2.40	4.60	109.6
14	GM	1.0	0.60	3.60 – 2.80 = 0.80	3.00	2.23	4.84	134.9

* CG) container glass; SG) sheet glass; LG) lamp glass; GM) glass mixture (33.0% SG + 33.0% SG + 33.0% LG; $\Delta t = 40°C$.

Thus, it is possible to obtain foam glass with a density of $175 - 200$ kg/m^3 based on various types of cullet. The main component of the mechanism of pore formation in foam glass is a viscous flow. By controlling the glass viscosity (the pore size) and the surface tension (the number of pores) using different means, it is possible to obtain foam glass with a lower density.

Foam-glass batches are complex multifactor objects of kinetic studies. However, the use of the proposed approach and evaluation parameters makes it possible to substantially simplify the investigation of the pore formation process in foam glass. It is possible to optimize the foam glass structure formation by satisfying the principle of the technological correlation between the rate of variation of the structural parameters (K_s, P, n, $1/n$, α_n, t) and the rate of the physicochemical processes accompanying pore formation (the type of glass and the gas-forming agent, the gas emission intensity, and the viscous flow intensity). The production of foam glass with preset properties requires maximum use of the opportunities of the physicochemical processes and ensuring their normal course.

REFERENCES

1. N. I. Min'ko, V. N. Bolotin, and N. F. Zhernovaya, Technological, energy, and environmental aspects of collection and utilization of glass cullet," *Steklo Keram.*, No. 5, 3 – 5 (1999).
2. I. I. Kitaigorodskii, N. N. Kachalov, V. V. Vargin., et al., *Glass Technology* [in Russian], Gosstroiizdat, Moscow (1951).
3. B. K. Demidovich and N. P. Sadchenko, *Foam Glass: Technology and Application, Issue 9* [in Russian], VNIIÉSM (1990).
4. V. A. Lotov, "Control of the structure-forming process in the technology of glass and silicate materials," *Steklo Keram.*, No. 5, 21 – 25 (1999).
5. V. A. Lotov, "Control of the structure formation process in porous materials," *Stroit. Mater.*, No. 9, 26 – 28 (2000).
6. F. Shill, *Foam Glass* [Russian translation], Stroiizdat, Moscow (1965).
7. V. V. Skorokhod, *Rheological Principles of Sintering Theory* [in Russian], Naukova Dumka, Kiev (1972).